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Solution-Processed PEDOT:PSS Films with Conductivities as Indium Tin Oxide through a Treatment with Mild and Weak Organic Acids

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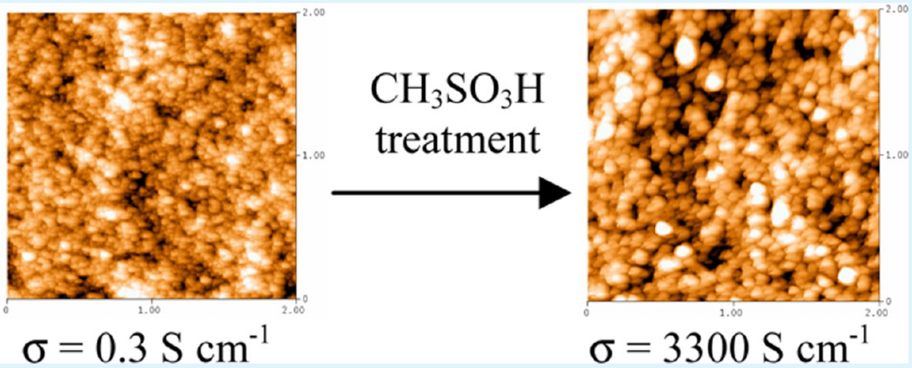

ABSTRACT: New transparent conductive materials are urgently needed for optoelectronic devices. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) will be a promising next-generation transparent electrode material if its conductivity is comparable to that of indium tin oxide (ITO). To enhance significantly the conductivity of PEDOT:PSS with mild compounds has practical significance. In this work, significant conductivity enhancements are achieved on PEDOT:PSS films after treatment with mild and weak organic acids. The treated PEDOT:PSS films exibit metallic behavior at room temperature. Their conductivity increases to about 3300 S cm^{-1} after they are treated with 8 M methanesulfonic acid. The conductivity enhancement depends on the acidity and physical properties of the organic acids. The mechanism for the conductivity enhancement is ascribed to proton transfer from the mild or weak organic acids to PSS^{-} of PEDOT:PSS. There are two factors for the proton transfer from mild or weak organic acids to PSS. One factor is the high acid concentration during the treatment, particularly after the vaporization of the water solvent. Another factor is the phase segregation of PSSH from PEDOT:PSS, because PSSH is hydrophilic, whereas PEDOT is hydrophobic. This method is better than that using very strong and corrosive acids like sulfuric acid. These highly conductive and highly transparent PEDOT:PSS films are promising for use as next-generation transparent electrodes.

KEYWORDS: *PEDOT:PSS, conductivity, methanesulfonic acid, phase segregation, protonation, conformation*

1. INTRODUCTION

Optoelectronic devices can convert light to electricity or electricity to light. They already have a huge market, and their market is still rapidly expanding. At least one transparent electrode is required for optoelectronic devices so that the devices can emit or harvest light. Indium tin oxide (ITO) is the conventional transparent electrode material of optoelectronic devices. However, ITO has several problems including the scarcity of indium on earth, the high price of indium, and its poor mechanical flexibility. Hence, ITO will have an availability problem in the long-term, and it can not be used as the electrode for flexible electronic devices.[1,2] Flexible electronic devices are regarded as next-generation electronic devices. Therefore, new transparent electrode materials are urgently needed. Many materials have been investigated for use as transparent electrode materials, such as conducting polymers,[3−15] carbon nanotubes,[16,17] graphenes,[18,19] and metal wire grids.[20−22] Among these materials, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, chemical structure shown in Scheme 1), a conducting polymer, is a promising candidate as a next-generation transparent electrode material.[23−25] PEDOT:PSS is the most successful conducting polymer in terms of its practical application. In comparison with other materials, PEDOT:PSS has advantages in processability, mechanical flexibility, and optical properties. It has good dispersibility in water and in some polar organic solvents. High-quality PEDOT:PSS films with a large area can be readily prepared by low-cost solution processing techniques such as coating and printing. Furthermore, PEDOT:PSS films are highly transparent in the visible range and highly mechanically flexible. Nevertheless, PEDOT:PSS does suffer from the problem of low conductivity. The conductivity of as-prepared PEDOT:PSS films from

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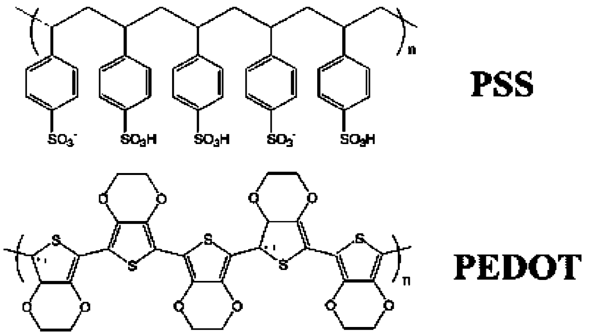
Scheme 1. Chemical Structure of PEDOT:PSS



aqueous solution is below 1 S cm^{-1}. This conductivity is lower than that of ITO by several orders in magnitude.

A couple of methods have been reported to enhance significantly the conductivity of PEDOT:PSS since the work by Kim et al.[26] They observed conductivity enhancement when dimethyl sulfoxide (DMSO) or dimethylformamide (DMF) was added into a PEDOT:PSS aqueous solution. Many other organic compounds, including ethylene glycol (EG), other polyols with two or more OH groups, anionic surfactants, ionic liquids, and dimethyl sulfate, were also investigated for the conductivity enhancement of PEDOT:PSS.[13,27−35] An alternative way to enhance the conductivity is the post-treatment of PEDOT:PSS films. Salts, polar organic compounds, carboxylic or inorganic acids, zwitterions, or cosolvents were investigated for the post-treatment of PEDOT:PSS films.[9,36−42] PEDOT:PSS aqueous solutions commercially supplied by H. C. Starck, which is now under Heraeus or Agfa, were used in those research works. The conductivity enhancement of the PEDOT:PSS films after a treatment depends on the grade of the PEDOT:PSS aqueous solutions.[43] A treatment of PEDOT:PSS films prepared from Clevios PH1000 with EG or DMSO can enhance the conductivity to about 680 S cm^{-1} or higher.[44] In 2011, Kim et al. observed a conductivity of 1418 S cm^{-1} on PEDOT:PSS films that were obtained from Clevios PH1000 solution added with EG and then treated in an EG bath.[45] When PEDOT:PSS films are treated with geminal diols, amphiphilic fluoro compounds, or alcohols, their conductivities are also higher than 1000 S cm^{-1}.[46−49]

It was recently observed that PEDOT:PSS films could have a conductivity of more than 3000 S cm^{-1} through a three-time post-treatment with sulfuric acid.[50] In addition, the sulfuric acid-treated PEDOT:PSS films exhibited metallic behavior from room temperature to 230 K. This conductivity is higher than that of ITO on plastic and is comparable to that of ITO on glass. Moreover, the acid treatment does not affect the transparency of PEDOT:PSS films in the visible range. These highly conductive and highly transparent PEDOT:PSS films have strong application potential as the transparent electrode of optoelectronic devices. However, sulfuric acid is a strong and corrosive acid, resulting in safety and environment concerns, particularly in industry. To use mild chemicals to significantly enhance the conductivity of PEDOT:PSS has practical significance. In this work, PEDOT:PSS films with a conductivity of more than 3000 S cm^{-1} were obtained through a treatment with methanesulfonic acid, a mild organic acid. Other mild or weak organic acids were also investigated to treat PEDOT:PSS films. The conductivity enhancement is related to the acidity and physical properties of the acids.

2. EXPERIMENTAL SECTION

2.1. Treatment of PEDOT:PSS Films with Acids. PEDOT:PSS aqueous solution (Clevios PH 1000) was purchased from H. C. Starck. PEDOT:PSS had a concentration of 1.3% by weight in the solution, and the PSS-to-PEDOT weight ratio was 2.5. All other chemicals were supplied from Sigma-Aldrich. Glass substrates were provided by Continental Lab. No further purification was carried out for all of these materials.

The glass substrates with a dimension of 1.3 × 1.3 cm^2 were cleaned sequentially with detergent, deionized (DI) water, acetone, and isopropyl alcohol. PEDOT:PSS films were prepared by spin coating the PEDOT:PSS aqueous solution on the glass substrates. The PEDOT:PSS films were dried at 110 °C on a hot plate for 40 min. The acid treatment was carried out by dropping 100 μL of acid solution on a PEDOT:PSS film at 160 °C on a hot plate. The films dried after about 5 min. They were then rinsed with DI water by immersing the PEDOT:PSS films into DI water for three times followed by drying at 160 °C.

2.2. Characterization of PEDOT:PSS Films. The conductivities of dried PEDOT:PSS films were measured by the van der Pauw four-point probe technique with a Keithley 2400 source/meter. Indium was pressed on the four corners of each PEDOT:PSS film on the glass substrate for the electrical contact. A Janis Research VPF-475 dewar with a Conductus LTC-11 temperature controller was used to study the temperature dependences of the resistivities of the untreated and treated PEDOT:PSS films. Liquid nitrogen was used as coolant. A Varian Cary 5000 UV−vis−NIR spectrometer was used to take the UV−vis−NIR absorption spectra of the polymer films. Quartz was used as the substrate for the PEDOT:PSS films for the UV−vis−NIR absorption spectroscopy, and a blank quartz sheet was used as the reference for the measurements. A Veeco NanoScope IV Multi-Mode AFM in the tapping mode was adopted to obtain the atomic force microscopic (AFM) images. An Axis Ultra DLD X-ray photoelectron spectrometer equipped with an Al Kα X-ray source (1486.6 eV) was used to collect the X-ray photoelectron spectra (XPS). An Alpha 500 step profiler was used to measure the thicknesses of the polymer films. The stylus force was 4.61 mg during the measurements. The thickness of the PEDOT:PSS films was 50 nm before and after acid treatment. Cyclic voltammograms (CV) were measured with an ECO Chemie

Table 1. Chemical Structure, Physical Properties, and Acidity of the Acids Used to Treat the PEDOT:PSS Films[a]

acid	chemical structure	T_m (°C)	T_b (°C)	pK_a	σ
methanesulfonic acid	CH_3SO_3H	17	167 (10 mm Hg)	−1.9	2870
malonic acid	$HOOCCH_2COOH$	135	decompose	2.83, 5.69	2210
oxalic acid	HOOCCOOH	189		1.25, 4.14	1900
pyruvic acid	$CH_3COCOOH$	11	165	2.50	1660
butyric acid	$CH_3CH_2CH_2COOH$	−8	164	4.82	740
acetic acid	CH_3COOH	16	118	4.76	450
water	H_2O	0	100	15.7	90

[a] The concentration of the acid solutions was 0.5 M. T_m, T_b, pK_a, and σ are the melting point, boiling point, acid dissociation constant, and conductivity, respectively.

Autolab PGSTAT 302N + FRA2 system. The working electrodes were prepared by dropping PEDOT:PSS aqueous solutions on Pt discs with a diameter of 2 mm, and the solution was dried at 120 °C. The counter and reference electrodes were Pt wire and Ag/AgCl (3 M NaCl), respectively. The solution was 0.1 M KCl aqueous solution. The scan rate was 50 mV s^{-1}.

3. RESULTS AND DISCUSSION

The PEDOT:PSS films were prepared by spin coating. The conductivity of pristine PEDOT:PSS films is about 0.3 S cm^{-1}.

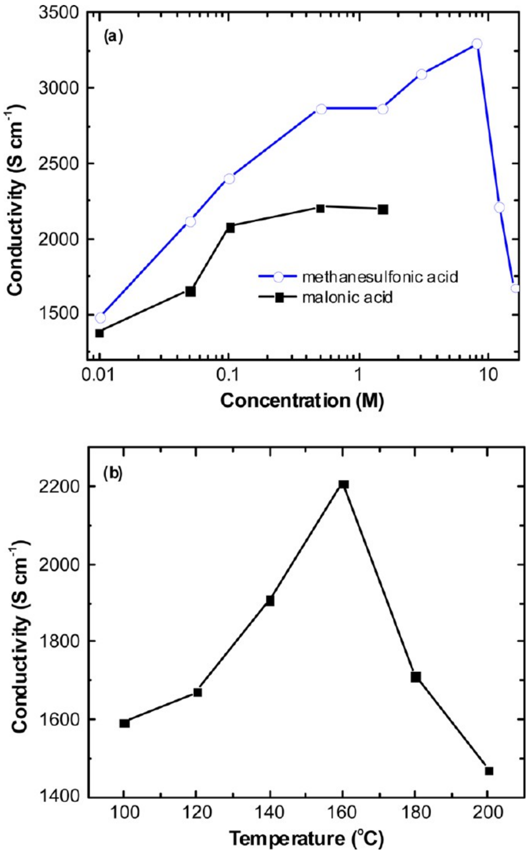


Figure 1. (a) Conductivities of PEDOT:PSS films after being treated with aqueous solutions of various malonic acid and methanesulfonic acid concentrations. The treatments were carried out at 160 °C. The inset is the chemical structure of PEDOT:PSS. (b) Conductivities of PEDOT:PSS films after being treated with 0.5 M malonic acid aqueous solutions at various temperatures.

The post-treatment was carried out by dropping an aqueous solution of 0.5 M organic acid at 160 °C for about 5 min. Water vaporized quickly at this temperature. After being rinsed with deionized water and dried at 160 °C, the conductivity of the PEDOT:PSS films was measured by the four-probe method. As shown in Table 1, the conductivity of PEDOT:PSS is significantly enhanced after an acid treatment, and the conductivity enhancement strongly depends on the acid used. After a treatment with 0.5 M methanesulfonic acid, the conductivity of the PEDOT:PSS films increased from 0.3 to 2870 S cm^{-1}. A treatment with 0.5 M malonic acid leads to a conductivity of 2210 S cm^{-1}. A treatment with oxalic acid or pyruvic acid also gives rise to a conductivity of more than 1600 S cm^{-1}. However, the conductivity enhancement is less significant when the PEDOT:PSS films were treated with butyric acid or acetic acid, reaching only 740 and 450 S cm^{-1}, respectively. Even a treatment with DI water can increase the conductivity of the PEDOT:PSS films.[51] The conductivity is 90 S cm^{-1} for the PEDOT:PSS films treated with water.

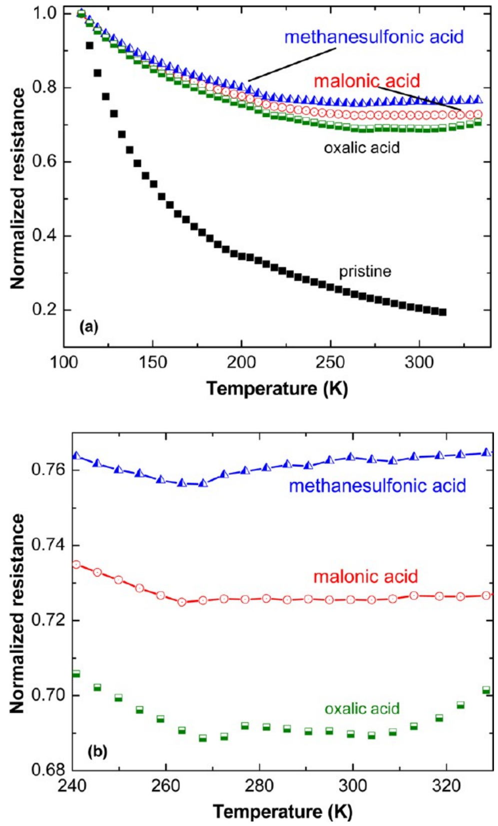


Figure 2. Temperature dependences of the normalized resistances of pristine and acid-treated PEDOT:PSS films. The concentration of the acid solutions is 0.5 M. (a) Normalized resistances versus temperature. (b) Temperature dependences of the resistances in the temperature range from 240 to 330 K.

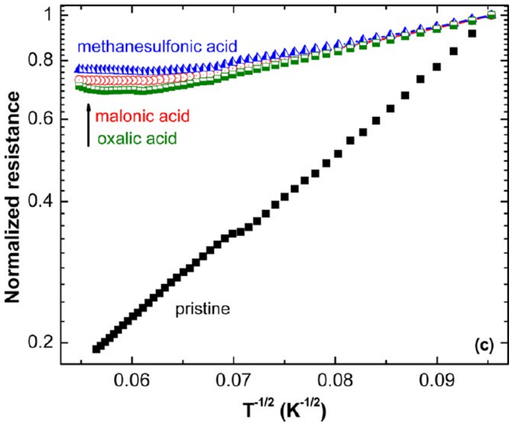


Figure 3. Analyses of the temperature dependences of the resistances with the 1D VRH model. The resistances are normalized to those of the corresponding PEDOT:PSS films at 110 K.

As shown in Table 1, the conductivity enhancement is generally consistent with the acid dissociation constant (pK_a) of the acids. On one hand, methanesulfonic acid has the lowest pK_a of −1.9, and it gives rise to the highest conductivity enhancement. On the other hand, butyric acid and acetic acid have the highest pK_a values, and they lead to a less significant conductivity enhancement. However, the conductivity values

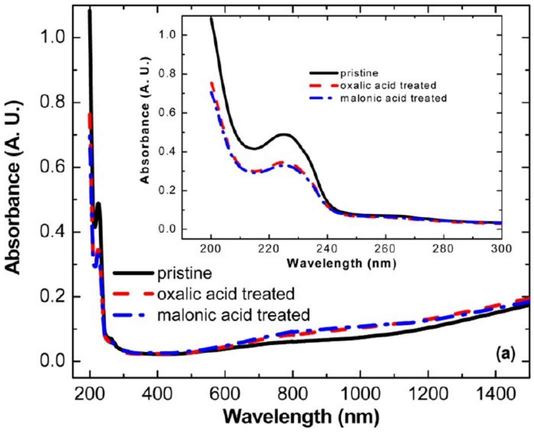


Figure 4. UV−vis−NIR absorption spectra of pristine and acid-treated PEDOT:PSS. The inset in panel a shows the magnified absorption spectra in the UV range. The concentration of the acid solutions is 0.5 M.

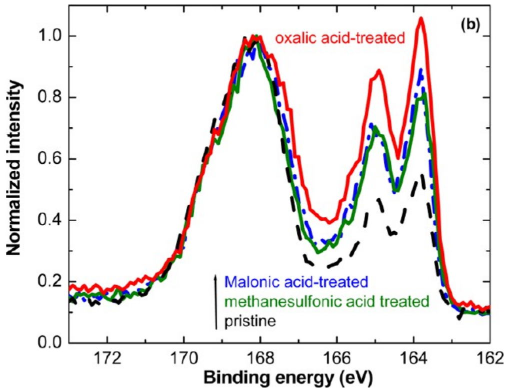


Figure 5. XPS of pristine and acid-treated PEDOT:PSS. The concentration of the acid solutions is 0.5 M.

presented in Table 1 indicate that pK_a is not the only factor for the conductivity enhancement. For example, the pK_{a1} value of malonic acid is greater than that of oxalic acid, but the former gives rise to more significant conductivity enhancement. This is related to their physical properties. During the treatment at 160 °C, malonic acid is in a liquid state, whereas oxalic acid is in a solid state after the vaporization of the water solvent. The liquid malonic acid uniformly wets the PEDOT:PSS films during the treatment, whereas the solid oxalic acid does not distribute on the PEDOT:PSS films uniformly but scatters on the surface. The solid oxalic acid cannot enhance the conductivity of the PEDOT:PSS films uniformly. This nonuniform conductivity enhancement also happens for the treatment with pyruvic acid. Although pyruvic acid is in a liquid state during the treatment, the pyruvic acid solution has poor wettability for PEDOT:PSS films. Hence, the treatment with pyruvic acid leads to less significant conductivity enhancement than that with malonic acid. The conductivity enhancement is also related to the boiling point of the acids. Although butyric acid has similar acidity to acetic acid, the former has a higher boiling point than the latter. Acetic acid disappears quickly during the treatment. The shorter remaining time of acetic acid is considered to be the reason for the less significant conductivity enhancement.

The different conductivity enhancements by different acids confirm that the conductivity-enhancement mechanism is related to the proton transfer from the acids to PSS^- of PEDOT:PSS.[50] After the PSS^- chains obtain protons, $PSS^- + H^+ \rightarrow PSSH$, they become neutral. Thus, the Coulombic attraction between the positively charge PEDOT chains and the negatively charge PSS^- chains disappears. This leads to a phase segregation of the neutral PSSH chains or segments from PEDOT:PSS, because PEDOT is hydrophobic, whereas PSSH is hydrophilic. Methanesulfonic acid has an acidity like PSSH, and other acids used in this work have a lower acidity than PSSH. There are two reasons for the occurrence of the proton transfer from these acids to PSS^-. One is the fact that these acids have a very high concentration during the treatment, particularly after the vaporization of the water solvent. Another reason is the phase segregation of neutral PSSH chains or segments from PEDOT:PSS as a consequence of the proton transfer, which is a driving force for the proton transfer. Thus, apart from the acidity, the boiling point of the acids also affects the conductivity enhancement. Acetic acid has a boiling point only slight higher than that of water. Hence, it gives rise to a less significant conductivity enhancement than butyric acid. Because methanesulfonic acid has the highest acidity and a boiling point higher than 160 °C, it gives rise to the highest conductivity enhancement among these acids.

The protonation of PSS^- is also evidenced by adding isopropyl alcohol into the malonic acid solution for the treatment. When there is 20% isopropyl alcohol (v/v) in 0.5 M malonic acid solution, the conductivity of the treated PEDOT:PSS film is only 1340 S cm^{-1}, remarkably lower than that of PEDOT:PSS treated with the 0.5 M malonic acid solution without isopropyl alcohol. This is because the presence of organic solvent suppresses the dissociation of malonic acid,[52] leading to a low proton concentration in the acid solution and less proton transfer from malonic acid to PSS^-.

It is also possible that ion exchange may happen between PSS^- and the anions of the acids.[53] SO_4^{2-} anions were observed in the PEDOT:PSS films after it was treated with sulfuric acid.[50] However, this kind of ion exchange does not remarkably affect the conductivity of the conducting polymer films.[53] The doping level of PEDOT:PSS may not change after the treatment because the acids used in this work are mild. They cannot oxidize or reduce PEDOT of PEDOT:PSS.

The experimental conditions during the acid treatment were investigated for the conductivity enhancement of the PEDOT:PSS films. Figure 1a presents the conductivities of PEDOT:PSS films after being treated with acids of different concentrations. When the PEDOT:PSS films were treated with 8 M methanesulfonic acid, the conductivity reached 3300 S cm^{-1}. The conductivity enhancement by methanesulfonic acid is even more significant than that by sulfuric acid, although the former has weaker acidity than the latter. The conductivity of the PEDOT:PSS films increases to about 1800 S cm^{-1} after they are treated with 0.5 M sulfuric acid.[50] Presumably, the reason for the higher conductivity after the treatment with methanesulfonic acid than with sulfuric acid is related to the defects in the PEDOT:PSS films generated during the acid treatment. Because sulfuric acid is much stronger than PSSH, the PEDOT:PSS films shrink saliently during the acid treatment so that breakdown of the PEDOT:PSS films can readily happen when the treatment time is long. This suggests that defects can exist in sulfuric acid-treated PEDOT:PSS films even when the films do not break down. The defects can lower the conductivity of the PEDOT:PSS films. In contrast, no breakdown was observed on the PEDOT:PSS films during the treatment with methanesulfonic acid even after a long time.

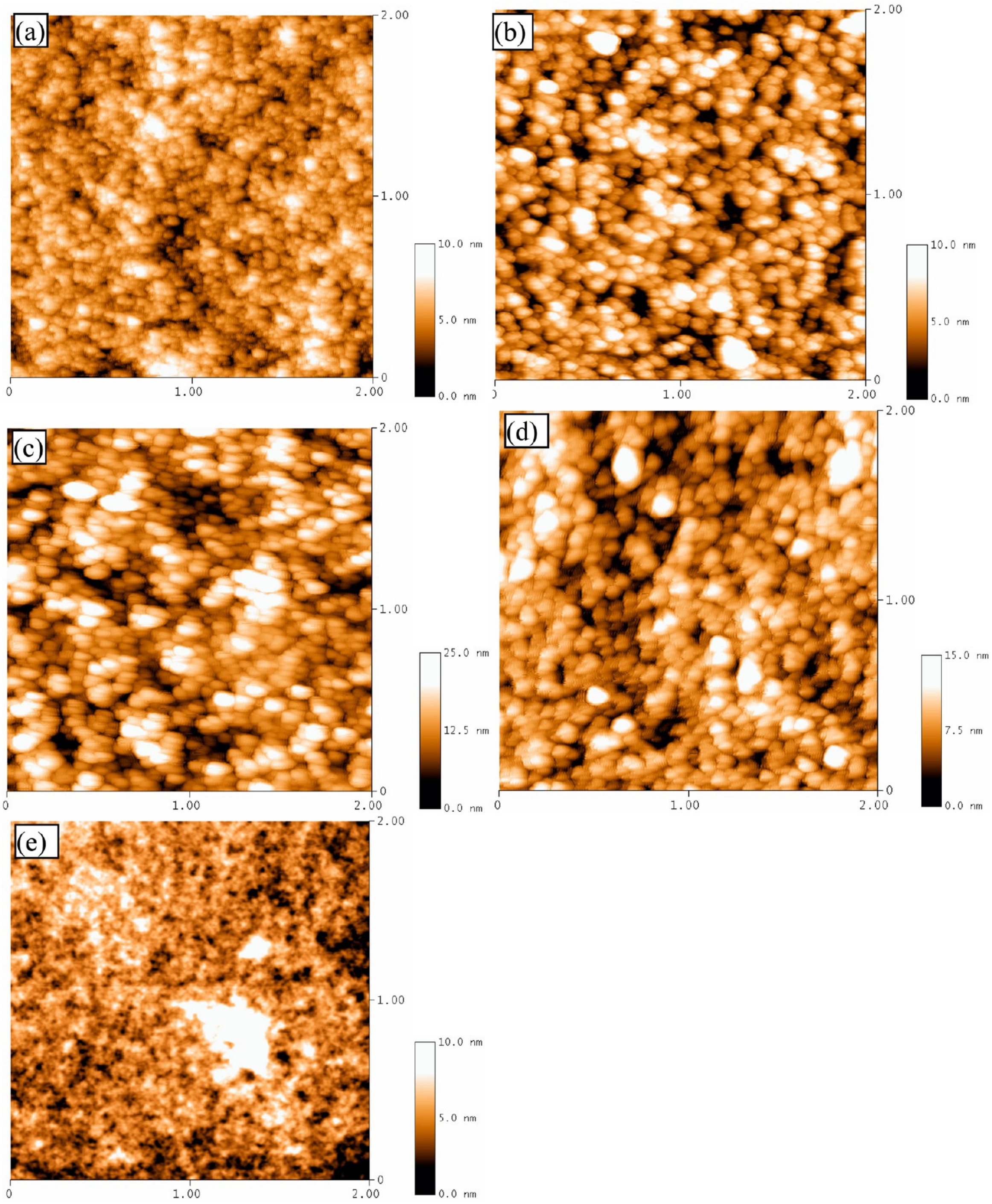


Figure 6. AFM images of PEDOT:PSS films (a) pristine and treated with (b) oxalic acid, (c) malonic acid, (d) methanesulfonic acid, and (e) DI water. The units for the AFM images are micrometers.

Therefore, there are fewer defects for the PEDOT:PSS films treated with methanesulfonic acid than with sulfuric acid.

The conductivities of the PEDOT:PSS films treated with aqueous solutions of various malonic acid concentrations are also presented in Figure 1a. At first, the conductivity increases with the increasing acid concentration. It then becomes flat when the concentration is higher than 0.5 M. The conductivity enhancement is also related to the temperature during the acid treatment (Figure 1b). The optimal temperature for the treatment is 160 °C. The optimal treating temperature should be related to the thermal properties of the PEDOT:PSS films.

The resistances of the PEDOT:PSS films treated with methanesulfonic acid, malonic acid, and oxalic acid were investigated from 320 to 110 K (Figure 2a). Although the resistances increases with the decrease of the temperature at the low-temperature range, they are almost insensitive to temperature or even increase with the increasing temperature when the temperature is higher than 270 K (Figure 2b). These temperature dependences of the resistances are saliently different from the behavior of the pristine PEDOT:PSS film, which shows a monotonic resistance increase with the decrease of the temperature in the whole temperature range.

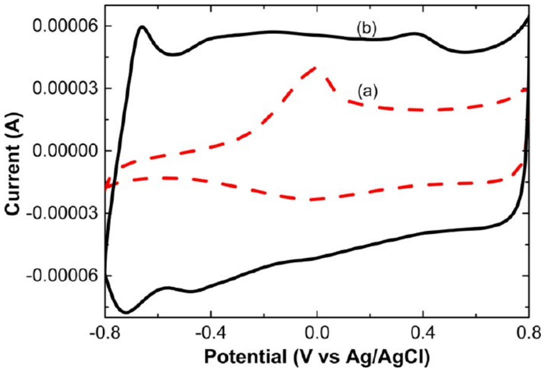


Figure 7. Cyclic voltammograms of (a) untreated and (b) 0.5 M methanesulfonic acid-treated PEDOT:PSS films in a 0.1 M KCl solution.

The temperature dependences of the resistances of conducting polymers are usually described by the 1D variable-range-hopping (VRH) model[26,54]

$$R(T) = R_0 \exp\left[\left(\frac{T_0}{T}\right)^{1/2}\right] \tag{1}$$

where $T_0 = 16/k_B N(E_F) L_{//} L_{\perp}^2$ is the energy barrier between localized states, $N(E_F)$ is the density of the states at the Fermi level, and $L_{//}$ ($L_{\perp}$) is the localization length in the parallel (perpendicular) direction. As shown in Figure 3, the resistances of the acid-treated PEDOT:PSS films agree with the 1D VRH model only at the low-temperature range. The T_0 values of the acid-treated PEDOT:PSS films at the low-temperature range and the pristine PEDOT:PSS film in the whole temperature range were obtained by analyzing the temperature dependences of the resistances by the 1D VRH model. They are 1903, 126, 100, and 84 K for the pristine, oxalic acid-treated, malonic acid-treated, and methanesulfonic acid-treated PEDOT:PSS films, respectively. The decrease in the T_0 value after the acid treatment suggests that the energy barrier for the charge transport is lowered.

The acid-treated PEDOT:PSS films were characterized by UV−vis−NIR absorption spectroscopy and XPS. The absorption in the infrared range becomes higher, whereas the intensities of the two absorption bands below 250 nm drop after the acid treatment (Figure 4). The absorption in the infrared range is related to the charge carriers, polarons, and bipolarons in PEDOT:PSS. The absorption increase suggests that the charge carriers become more delocalized on the PEDOT chains after the acid treatment. The absorption bands in the UV range originate from the aromatic rings of PSS. The lower absorption intensity of PSS indicates that some PSSH chains are removed from the PEDOT:PSS films after an acid treatment. The removal of some PSSH chains from the PEDOT:PSS films after an acid treatment is supported by the XPS spectra of the PEDOT:PSS films (Figure 5). The two XPS bands with the binding energies between 166 and 172 eV originate from the sulfur atoms of PSS, and the two XPS bands with the binding energies between 162 and 166 eV are due to the sulfur atoms of PEDOT.[55,56] The S 2p XPS intensity ratio of PEDOT to PSS increases after an acid treatment. These spectra also indicate that the acid treatment leads to less PSS in the PEDOT:PSS films.

The acid treatment can affect the morphology of the PEDOT:PSS films. Apart from the removal of some PSSH chains, it can also give rise to the conformational change of the PEDOT chains. The PEDOT chains have to adopt a coil conformation in water because of the Coulombic attraction between PEDOT and PSS. This coil conformation is reserved in the solid PEDOT:PSS films. However, PEDOT has a rigid conjugated π structure, and its favored conformation is the linear or extended-coil structure. The removal of the some PSSH chains can cause the conformational change of PEDOT from the coil structure to the extended-coil or linear structures. The effect of the acid treatment on the morphology PEDOT:PSS films was confirmed by AFM (Figure 6). The grains become larger after acid treatment. This morphological change is similar to the treatment of PEDOT:PSS films by methanol, as reported by Chu et al., but different from that of the treatment with a strong acid like sulfuric acid.[46−50] The grain size is about 50 nm for the pristine PEDOT:PSS films, and it increases to about 100 nm after acid treatment. The roughness of the untreated PEDOT:PSS film is 3.2 nm. It increases to 3.6, 3.7, and 4.0 nm after treatment with oxalic acid, malonic acid, and methanesulfonic acid, respectively. The surface morphology of the PEDOT:PSS films treated with water becomes even smoother; the roughness is decreased to 2.9 nm.

The acid-induced change in the conformation of the polymer chains were further confirmed by the cyclic voltammetry of the PEDOT:PSS films before and after the acid treatment. It has been revealed that the electrochemical activity of PEDOT:PSS is quite sensitive to the conformation of the PEDOT chains.[29] New electrochemical activity appears at a low electrochemical potential range after the PEDOT chains change from a coil conformation to an extended-coil or linear conformation. As shown in Figure 7, the electrochemical activity of the PEDOT:PSS films significantly increases in the electrochemical range of −0.8 to 0.8 V versus Ag/AgCl after the treatment with methanesulfonic acid. Moreover, there is almost no electrochemical activity at potential lower than −0.4 V versus Ag/AgCl for the pristine PEDOT:PSS films, whereas remarkable redox process can be observed in this range after the acid treatment.

4. CONCLUSIONS

Weak or mild organic acids can significantly enhance the conductivity of PEDOT:PSS films. The conductivity of PEDOT:PSS films increases from 0.3 to 3300 S cm^{-1} after a treatment with 8 M methanesulfonic acid. The acid-treated PEDOT:PSS films exhibit metallic behavior at room temperature. The conductivity enhancement is related to the acidity and physical properties of the acids. The conductivity enhancement is attributed to the protonation of PSS chains, which leads to the phase segregation of some PSSH chains from PEDOT:PSS and conformational change of PEDOT chains from a coil to an extended-coil or linear structure. There are two factors for the proton transfer from the mild or weak organic acids to PSS$^-$. One factor is the high concentration of the acids during the treatment after the vaporization of the water solvent. Another factor is the phase segregation of neutral PSSH chains or segments from PEDOT:PSS, because PSSH is hydrophilic, whereas PEDOT is hydrophobic. Although the conductivity enhancement is comparable to that using surfuric acid, this method has an advantage because mild and weak acids are used.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Inganäs, O. *Nat. Photonics* **2011**, *5*, 201−202.
(2) Chipman, A. *Nature* **2007**, *449*, 131−131.
(3) Na, S. I.; Kim, S. S.; Jo, J.; Kim, D. Y. *Adv. Mater.* **2008**, *20*, 4061−4067.
(4) Kim, W. H. *Appl. Phys. Lett.* **2002**, *80*, 3844−3846.
(5) Zhang, F.; Johansson, M.; Andersson, M. R.; Hummelen, J. C.; Inganäs, O. *Adv. Mater.* **2002**, *14*, 662−665.
(6) Lee, C. S.; Kim, J. Y.; Lee, D. E.; Koo, Y. K.; Joo, J.; Han, S.; Beag, Y. W.; Koh, S. K. *Synth. Met.* **2003**, *135*, 13−14.
(7) Argun, A. A.; Cirpan, A.; Reynolds, J. R. *Adv. Mater.* **2003**, *15*, 1338−1341.
(8) Ouyang, J.; Chu, C. W.; Chen, F. C.; Xu, Q.; Yang, Y. *Adv. Funct. Mater.* **2005**, *15*, 203−208.
(9) Ouyang, J.; Yang, Y. *Adv. Mater.* **2006**, *18*, 2141−2144.
(10) Yoo, J. E.; Yoo, J. E.; Lee, K. S.; Garcia, A.; Tarver, J.; Gomez, E. D.; Baldwin, K.; Sun, Y.; Meng, H.; Nguyen, T. Q.; Loo, Y. L. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 5712−5717.
(11) Huang, J. H.; Kekuda, D.; Chu, C. W.; Ho, K. C. *J. Mater. Chem.* **2009**, *19*, 3704−3712.
(12) Na, S. I.; Wang, G.; Kim, S. S.; Kim, T. W.; Oh, S. H.; Yu, B. K.; Lee, T.; Kim, D. Y. *J. Mater. Chem.* **2009**, *19*, 9045−9053.
(13) Hsiao, Y. S.; Whang, W. T.; Chen, C. P.; Chen, Y. C. *J. Mater. Chem.* **2008**, *18*, 5948−5955.
(14) Chang, Y. M.; Wang, L.; Su, W. F. *Org. Electron.* **2008**, *9*, 968−973.
(15) Lee, M. W.; Lee, M. Y.; Choi, J. C.; Park, J. S.; Song, C. K. *Org. Electron.* **2010**, *11*, 854−859.
(16) Gruner, G. *J. Mater. Chem.* **2006**, *16*, 3533−3539.
(17) Mei, X.; Ouyang, J. *J. Mater. Chem.* **2011**, *21*, 17842−17849.
(18) Kim, K. S.; Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J. H.; Kim, P.; Choi, J. Y.; Hong, B. H. *Nature* **2009**, *457*, 706−710.
(19) Becerril, H. A.; Mao, J.; Liu, Z.; Stoltenberg, R. M.; Bao, Z.; Chen, Y. *ACS Nano* **2008**, *2*, 463−470.
(20) Lee, J. Y.; Connor, S. T.; Cui, Y.; Peumans, P. *Nano Lett.* **2008**, *8*, 689−692.
(21) Yu, Z.; Zhang, Q.; Li, L.; Chen, Q.; Niu, X.; Liu, J.; Pei, Q. *Adv. Mater.* **2011**, *23*, 664−668.
(22) Yu, Z.; Li, L.; Zhang, Q.; Hu, W.; Pei, Q. *Adv. Mater.* **2011**, *23*, 4453−4457.
(23) Groenendaal, L.; Jonas, F.; Freitag, D.; Peilartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481−494.
(24) Pei, Q.; Zuccarello, G.; Ahlskogt, M.; Inganäs, O. *Polymer* **1994**, *35*, 1347−1351.
(25) Ouyang, J. *Displays* **2013**, *34*, 423−436.
(26) Kim, J. Y.; Jung, J. H.; Lee, D. E.; Joo, J. *Synth. Met.* **2002**, *126*, 311−316.
(27) Pettersson, L. A. A.; Ghosh, S.; Inganäs, O. *Org. Electron.* **2002**, *3*, 143−148.
(28) Jönsson, S. K. M.; Birgersonb, J.; Crispin, X.; Greczynskib, G.; Osikowiczb, W.; Denier van der Gonc, A. W.; Salaneckb, W. R.; Fahlman, M. *Synth. Met.* **2003**, *139*, 1−10.
(29) Ouyang, J.; Xu, Q.; Chu, C. W.; Yang, Y.; Li, G.; Shinar, J. *Polymer* **2004**, *85*, 8443−8450.
(30) Crispin, X.; Jakobsson, F. L. E.; Crispin, A.; Grim, P. C. M.; Andersson, P.; Volodin, A.; van Haesendonck, C.; van der Auweraer, M.; Salaneck, W. R.; Berggren, M. *Chem. Mater.* **2006**, *18*, 4354−4360.
(31) Nardes, A. M.; Kemerinka, M.; de Kokb, M. M.; Vinkenc, E.; Maturovaa, K.; Janssen, R. A. J. *Org. Electron.* **2008**, *9*, 727−734.
(32) Nardes, A. M.; Janssen, A. J. R.; Kemerink, M. A. *Adv. Funct. Mater.* **2008**, *18*, 865−871.
(33) Döbbelin, M.; Marcilla, R.; Salsamendi, M.; Pozo-Gonzalo, C.; Carrasco, P. M.; Pomposo, J. A.; Mecerreyes, D. *Chem. Mater.* **2007**, *19*, 2147−2149.
(34) Fan, B. H.; Mei, X. G.; Ouyang, J. *Macromolecules* **2008**, *41*, 5971−5973.
(35) Reyes-Reyes, M.; Cruz-Cruz, I.; Lopez-Sandoval, R. *J. Phys. Chem. C* **2010**, *114*, 20220−20224.
(36) Xia, Y.; Ouyang, J. *ACS Appl. Mater. Interfaces* **2010**, *2*, 474−483.
(37) Xia, Y.; Ouyang, J. *Macromolecules* **2009**, *42*, 4141−4147.
(38) Xia, Y.; Ouyang, J. *Org. Electron.* **2010**, *11*, 1129−1135.
(39) Xia, Y.; Zhang, H. M.; Ouyang, J. *J. Mater. Chem.* **2010**, *20*, 9740−9747.
(40) Xia, Y.; Ouyang, J. *J. Mater. Chem.* **2011**, *21*, 4927−4936.
(41) Sun, K.; Xia, Y.; Ouyang, J. *Sol. Energy Mater. Sol. Cells* **2012**, *97*, 89−96.
(42) Peng, B.; Guo, X.; Cui, C.; Zou, Y.; Pan, C.; Li, Y. *Appl. Phys. Lett.* **2011**, *98*, 243308-1−243308-3.
(43) Xia, Y.; Ouyang, J. *ACS Appl. Mater. Interfaces* **2012**, *4*, 4131−4139.
(44) Zhou, Y.; Cheun, H.; Choi, S.; Potscavage, W. J.; Fuentes-Hernandez, C.; Kippelen, B. *Appl. Phys. Lett.* **2007**, *97*, 153304-1−153304-3.
(45) Kim, Y. H.; Sachse, C.; Machala, M. L.; May, C.; Müller-Meskamp, L.; Leo, K. *Adv. Funct. Mater.* **2011**, *21*, 1076−1081.
(46) Xia, Y.; Sun, K.; Ouyang, J. *Energy Environ. Sci.* **2012**, *5*, 5325−5332.
(47) Xia, Y.; Ouyang, J. *Org. Electron.* **2012**, *13*, 1785−1792.
(48) Alemu, D.; Wei, H. Y.; Ho, K. C.; Chu, C. W. *Energy Environ. Sci.* **2012**, *5*, 9662−9671.
(49) Mengistie, D. A.; Wang, P. C.; Chu, C. W. *J. Mater. Chem. A* **2013**, *1*, 9907−9915.
(50) Xia, Y.; Sun, K.; Ouyang, J. *Adv. Mater.* **2012**, *24*, 2436−2440.
(51) DeLongchamp, D. M.; Vogt, B. D.; Brooks, C. M.; Kano, K.; Obrzut, J.; Richter, C. A.; Kirillov, O. A.; Lin, E. K. *Langmuir* **2005**, *21*, 11480−11483.
(52) Yasuda, M. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 429−432.
(53) Li, Y.; Ouyang, J.; Yang, J. *Synth. Met.* **1995**, *74*, 49−53.
(54) Joo, J.; Long, S. M.; Pouget, J. P.; Oh, E. J.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1998**, *57*, 9567−9580.
(55) Voigt, U.; Jaeger, W.; Findenegg, G. H.; Klitzing, R. V. *J. Phys. Chem. B* **2003**, *107*, 5273−5280.
(56) Crispin, X.; Marciniak, S.; Osikowicz, W.; Zotti, G.; Denier van der Gon, A. W.; Louwet, F.; Fahlman, M.; Groenendaal, L.; De Schryver, F.; Salaneck, W. R. *J. Polym. Sci., Part A-2* **2003**, *41*, 2561−2583.